Identification and Characterization of Corrosion Scale of Cooler Heat Exchanger

by

Muhammad Syaril Azril Bin Ibrahim

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Mechanical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Universiti Teknologi PETRONAS
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BACHELOR OF ENGINEERING (Hons)
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Approved by,

____

(AP Ir Dr Mokhtar Che Ismail)

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TRONOH, PERAK

May 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MUHAMMAD SYARIL AZRIL BIN IBRAHIM

Abstract

The formation of hard scale due to cooling water corrosion has significant effect in reducing the heat transfer performance and integrity of heat exchanger. The objectives of this study are to identify the corrosion products of the internal heat exchanger tube, to characterize the mechanical and chemical properties of rust products in order to propose better cleaning method. The sample was obtained from PETRONAS refinery plant which then been cut and analysed. The identification of the corrosion products by X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM)/Energy Dispersive X-ray Spectroscopy (EDX). Mechanical properties for the corrosion products are characterized using Vickers microhardness test and the dissolution of rust scale or the cleaning methods for the characterization of the chemical properties. The results found from XRD are Iron oxide Fe_2O_3, Hematite α-Fe_2O_3, Lepidocrocite γ-Fe_2O_3 / $Fe_2O_3.H_2O$ / Fe + 3O(OH), Goethite α-FeOOH / $Fe_2O_3.H_2O$ and Magnetite Fe_3O_4. Moreover, Goethite α-FeOOH (cotton ball), Lepidocrocite γ-FeOOH (fine crystal plate), cracking and flaking are found with FESEM and EDX approved the existence of their elements. From the hardness test, the hardness value found is 110HV. The corrosion scale was successfully removed by using industrial FOVAC F315 Rust Remover. In conclusion, laboratory characterization of corrosion scale can assist plant operator to provide better heat exchanger cleaning procedure.

Acknowledgments

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CHAPTER 1: INTRODUCTION

1.1 Background

Heat exchanger is an important equipment in oil refinery plant. There are many type of heat exchangers available and one of it is a shell and tube heat exchanger. It is the mechanical device which is specially used for transfer the thermal energy between two or more fluids at differing temperatures and in thermal contact.

For some application, cooling water is used as a cooling medium. However, cooling water leads to the corrosion, formation of hard scale and leakage of the heat exchanger tube. When the scale is formed, it will affect the thermal efficiency and reduce the efficiency of the heat exchanger. In addition, when there is a leaking or a metal loss in the heat exchanger tube, besides affecting the efficiency, it will affect the integrity and safety of the whole plant. When there is a leaking, there are high chances for shell product which mainly hydrocarbon to enter the cooling water distribution system and ignite fire with presence of any spark.

The tubes are normally cleaned by hydrojet during shutdown but the result of the hydrojet cleaning is not satisfactory.

1.2 Problem Statement

The formation of hard scale due to cooling water corrosion has significant effect in reducing the performance and integrity in heat transfer in heat exchanger. Hence, efficient cleaning during shutdown is critical to ensure optimum performance of the heat exchanger.

1.3 Objectives and Scope of Study

The objectives of this study are to identify the corrosion products of the internal heat exchanger tube due to cooling water, characterize the mechanical and chemical properties and study the efficient cleaning method.

The scopes of this study are to:

(1) Identify & characterize corrosion scale morphology and its properties.

(2) Investigate the cleaning method for internal heat exchanger tubes due to cooling water corrosion by different techniques and cleaning agents.

CHAPTER 2: LITERATURE REVIEW AND/OR THEORY

2.1 Heat Exchanger in oil refinery

In typical oil refinery plant, many heat exchangers are used to cool hydrocarbon products. A **shell and tube heat exchanger** [1] is a class of the heat exchanger. It is the most common type of heat exchanger in oil refineries and other large chemical processes, and is suited for higher-pressure and or/temperature applications. As its name implies, this type of heat exchanger consists of a shell (a large pressure vessel) with a bundle of tubes inside it. One fluid runs through the tubes, and another fluid flows over the tubes (through the shell) to transfer heat between the two fluids. The set of tubes is called a tube bundle, and may be composed of several types of tubes: plain, longitudinally finned, etc.

There are many available type of heat exchangers such shell and tube, plate, spiral and double pipe, however the type of heat exchanger been used in this study is shell and tube heat exchanger. According to Tubular Exchanger Manufacturers Association (TEMA), type designation for each exchanger is described in Figure 2.1 [2].

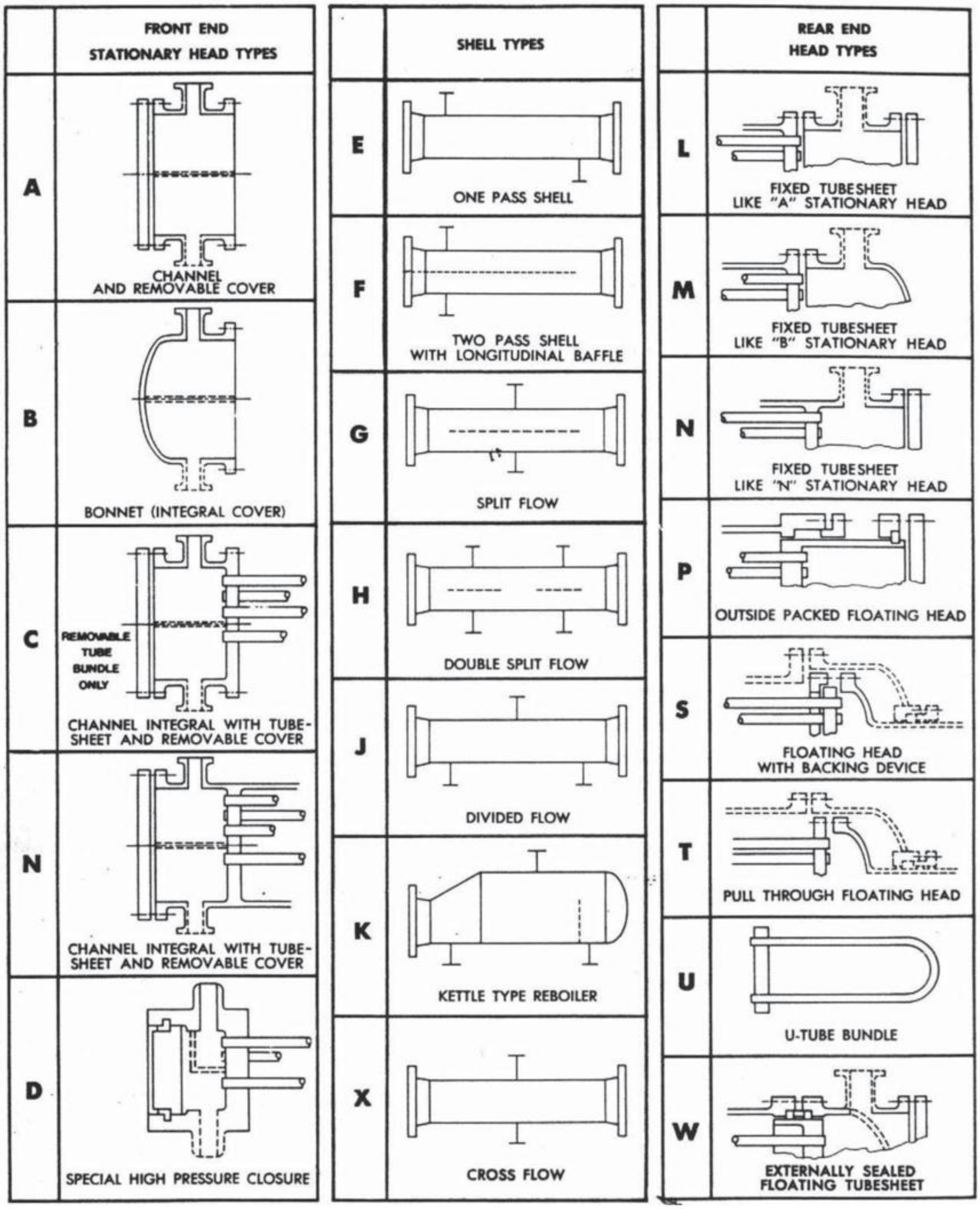


Figure 2. 1: Type designation of shell and tube heat exchanger

2.2 Cooler Heat Exchanger

Heat Exchangers can be classified according to their service [3]. Basically, a service may be single-phase (such as the cooling or heating of a liquid or gas) or two-phase (such as condensing or vaporizing). Since there are two sides to an STHE, this can lead to several combinations of services. Broadly, services can be classified as follows: single-phase (both shellside and tubeside); condensing (one side condensing and the other single-phase); vaporizing (one side vaporizing and the other side single-phase); and condensing/vaporizing (one side condensing and the other side vaporizing).

The following nomenclature is usually used: *Heat exchanger:* both sides single-phase and process streams (that is, not a utility). *Cooler:* one stream a process fluid and the other cooling water or air. *Heater:* one stream a process fluid and the other a hot utility, such as steam or hot oil. *Condenser:* one stream a condensing vapour and the other cooling water or air. *Chiller:* one stream a process fluid being condensed at sub-atmospheric temperatures and the other a boiling refrigerant or process stream. *Reboiler:* one stream a bottoms stream from a distillation column and the other a hot utility (steam or hot oil) or a process stream.

Cooling water is used directly or indirectly to cool chemical products, steel products, etc. Generally, cooling water is used indirectly to cool process fluids (liquids and gases) through heat exchangers. This system is called an indirect cooling system. Solid products are often cooled directly by spraying water through nozzles. This system is termed a direct cooling system and is used in plants handling solid products, such as iron works and food factories. Cooling water systems [4] are classified as shown in Table 2.1 and the flow diagrams for each indirect cooling water system are shown in Figure 2.2, Figure 2.3 and Figure 2.4 respectively.

Table 2. 1: Classification of Cooling Water Systems

Cooling water system	Indirect cooling water system	Open recirculating cooling water system
		Closed recirculating cooling water system
		Once through cooling water system
	Direct cooling water system	Open recirculating cooling water system
		Once through cooling water system

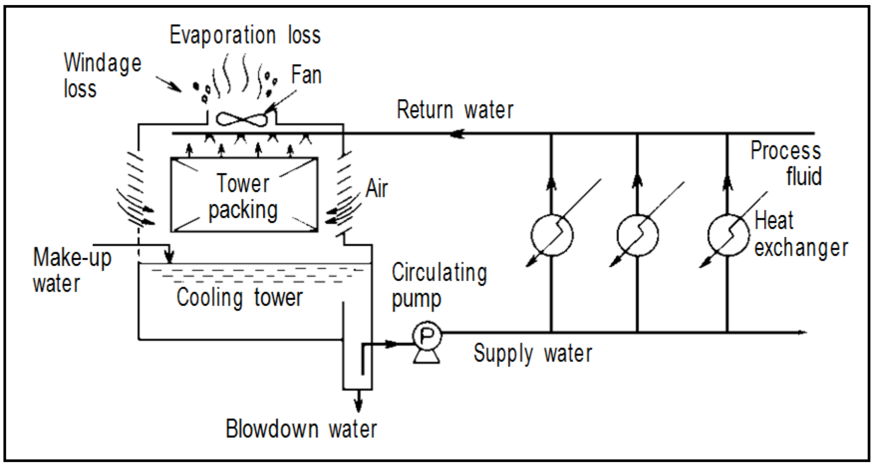


Figure 2. 2: Flow diagram of an open recirculating cooling water system

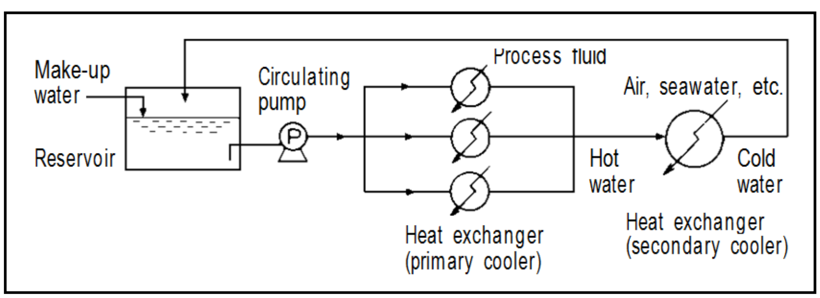


Figure 2. 3: Flow diagram of a closed recirculating cooling water system

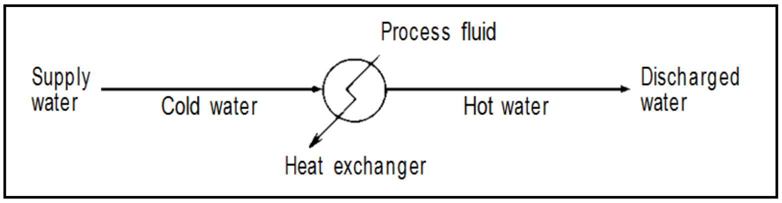


Figure 2. 4: Flow diagram of an once through cooling water system

2.3 Heat Exchanger Fouling

The formation of fouling inside the exchanger tube will affect the thermal efficiency of the heat exchanger. The major fouling mechanisms [5] are precipitation fouling, particulate fouling, chemical reaction fouling, corrosion fouling and biological fouling.

The calculation of the overall heat transfer coefficient contains the terms to account for the thermal resistances of the fouling layers on the inside and outside heat transfer surfaces. These fouling layers are known to increase in thickness with time as the heat exchanger is operated. Fouling layers normally have a lower thermal conductivity than the fluids or the tube material, thereby increasing the overall thermal resistance.

Beside the formation of scale that block the heat exchanger tube, the leakage of tube due to corrosion may contribute to decrease in thermal efficiency and will affect the safety and integrity of the oil refinery plant.

The performance of heat exchangers usually deteriorates with time as a result of accumulation of *deposits* on heat transfer surfaces. The layer of deposits represents *additional resistance* to heat transfer and causes the rate of heat transfer in a heat exchanger to decrease. The net effect of these accumulations on heat transfer is represented by a **fouling factor [**6**]** R_f, which is a measure of the *thermal resistance* introduced by fouling.

The most common type of fouling is the *precipitation* of solid deposits in a fluid on the heat transfer surfaces. The scales of such deposits come off by scratching, and the surfaces can be cleaned of such deposits by chemical treatment. Another form of fouling, which is common in the chemical process industry, is *corrosion* and other *chemical fouling.* In this case, the surfaces are fouled by the accumulation of the products of chemical reactions on the surfaces.

Heat exchangers may also be fouled by the growth of algae in warm fluids. This type of fouling is called *biological fouling* and can be prevented by chemical treatment.

The fouling factor is obviously zero for a new heat exchanger and increases with time as the solid deposits build up on the heat exchanger surface. The fouling factor depends on the *operating temperature* and the *velocity* of the fluids, as well as the length of service. Fouling increases with *increasing temperature* and *decreasing velocity*.

2.4 Cooling Water Corrosion

Generally, cooling water is used indirectly to cool process fluids (liquids and gases) through heat exchangers. Utilization of cooling water causes the concentration of dissolved solids, resulting in the frequent problems with corrosion, scale and slime (biofouling) in cooling water systems.

Corrosion fouling is among the type of fouling , at which iron oxide, the most common form of corrosion product, is the result of an electro-chemical reaction and forms as a scale on iron-containing, exposed surfaces of the heat exchanger. This scale produces an added thermal resistance to the base metal of the heat transfer surface.

Problems occurred in cooling water systems are generally classified into the following three categories: corrosion, scale and biofouling (slime and sludge). Hence, in this study, the corrosion which occurred in cooling water system is the problem of the interest.

In basic corrosion mechanism, it involved anodic and cathodic reactions. Iron reacts with dissolve oxygen in the cooling water to form ferrous hydroxide, which is further oxidized to ferric hydroxide.

$$Fe + \frac{1}{2} O_2 + H_2o = Fe(OH)_2 \qquad (1)$$

$$2Fe(OH)_2 + \frac{1}{2} O_2 + H_2O = 2Fe(OH)_3 \qquad (2)$$

Aqueous corrosion is an electrochemical process. That is, the overall reaction involves an oxidation of one chemical species (in this case, iron), a reduction of a second species (dissolved oxygen), and a transfer of electrons through the medium (water and metal) between the two species. Figure 2.5 [7] shows the corrosion reactions of carbon steel in neutral water.

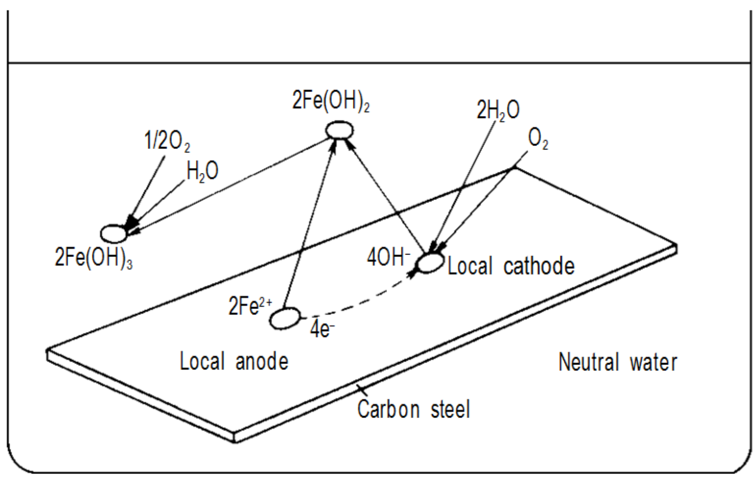


Figure 2. 5: Corrosion reactions of carbon steel in neutral water

Corrosion shortens the lives of the equipments in cooling systems and causes leakage of the products or the cooling water from the heat exchangers. Table 2.2 [8] below shows common troubles occurred in cooling water systems and their causes.

Table 2. 2: Troubles occurred in cooling water systems and their causes

Trouble	Cause
1) Shortened operation lives of heat exchanger, pipings, etc.	a) Corrosion b) Corrosion occurred under deposits such as slime

	and sludge c) Corrosion under porous scale
2) Reduction of heat exchanger thermal efficiency	a) Adhesion of corrosion product, scale and slime b) Accumulation of sludge
3) Increase of pressure drop and reduction of cooling water circulation rate in system (increase in electric power consumption of pumps)	a) Adhesion of corrosion product, scale and slime b) Accumulation of sludge c) Tube clogging with foreign matters
4) Leakage of products and contamination of products with cooling water	a) Penetration of heat exchanger tube by corrosion and under deposit corrosion
5) Adsorption and waste of water treatment chemicals	a) By corrosion products, scale, slime and sludge b)By suspended solids in cooling water

The adhesion of corrosion products also causes problems such as the reduction of heat exchanger thermal efficiency and water circulation rate. Scale deposition and slime adhesion in heat exchangers not only lower the thermal efficiency but also frequently cause local corrosion under the deposits.

These problems scarcely occur independently and are usually caused with a mutual relationship. Table 2.3 shows the frequency of these problems in each type of cooling water system. The problems occur most frequently in open recirculating cooling water systems, since the dissolved solids are concentrated in the cooling water by the water evaporation.

Table 2. 3: Frequency of trouble occurrence in each type of cooling water systems

Type of cooling water system / Problems	Once through	Closed re-circulating	Open re-circulating
Corrosion	○	◎	◎
Scale	△	△	◎
Slime	○	△	◎

Note: Frequency of problems ◎ (higher)← ○ → △(lower)

2.5 Identification and Characterization of Corrosion Product

The atmospheric corrosion of steel is an extensive topic that has been studied by many authors. From the identification of corrosion product, the two phases that always present are lepidocrocite (γ-FeOOH) and goethite (α-FeOOH), in this order in terms of content in the rust. Other phases that usually present in the steel corrosion products are magnetite (Fe_3O_4) or maghemite ($\gamma-$Fe2O3), which cannot be differentiated by XRD due to their similar crystalline structure. Fuente, Simancas, and Morcillo (2011) [9] point that the identification of the typical morphological structures of the corrosion products are lepidocrocite (sandy crystals and flowery plates), goethite (cotton balls structures) and akaganeite (cotton balls structures and cigar-shaped crystals). This work also has similarities in result with AntunesI, CostaI, and FariaII's (2003) research [10].

Kamimura , Hara , Miyuki , Yamashita , and Uchida (2006) [11] report that it is well known that the rust is composed of mainly ferric oxyhydroxides (FeOOH) and an X-ray amorphous substance, which gives no clear peak by the X-ray diffraction technique. It is reported that different structures of oxyhydroxides such as α-FeOOH, γ-FeOOH and β-FeOOH are formed, and in some cases spinel type of iron oxides such as magnetite (Fe_3O_4) are contained in the rust layer depending on environmental condition. There are many research which had been done on the identification of corrosion products [12], [13], [14],[15], most of the results shown that the identified corrosion products are lepidocrocite (γ-FeOOH) , goethite (α-FeOOH), akaganeite (β-FeOOH) and magnetite (Fe_3O_4).

Hardness is the measure of how resistant a material is to deformation of the surface under a specified load. Stronger materials will have greater resistance to deformation than weaker materials, so hardness testing is often used as an approximate means of gauging the relative strength of materials. Hardness testing is used to characterize the mechanical properties of the corrosion scale. This can be relate to the pressure required during hydro jet cleaning for best and efficient strength to remove all the hard corrosion scale which deposited in the internal tube of heat exchanger.

However, micro hardness of the corrosion products layer are not widely studied among researchers. One micromechanical study of corrosion products layers [16] found that the micro-indentation tests reveal local elastic modulus values of corrosion products layers comprised between 50 and 200 GPa. Next, K. Gao and his team [17] had studied the mechanical properties of CO_2 corrosion product scales and their relationship to corrosion rates. They found the Young's modulus, E of the scale, measured by nano-indentation test. The average values of E were 104.3 GPa, 100.3 GPa and 111.4 GPa for scales formed under static conditions or with a flow rate of 0.5 m/s and 1.0 m/s, respectively. Next, Y. Isshiki, J. Shi, H. Nakai and M.Hashimoto [18] studied on microhardness and corrosive properties of stainless steel 304 and stated in their paper that few samples are either smooth depth profile, fluctuate rather and heavily fluctuated depth profile of micro hardness.

2.6 Cleaning Methods

Most heat exchangers are cleaned offline. The types of offline cleaning methods are mechanical, hydraulic, and chemical.

For U-tube removable-bundle units, the ability to clean the tube side mechanically is limited by the smallest bend radius [19]. Most U-tube units can be cleaned hydraulically with special jets and lances. However, where the hydraulic equipment cannot transverse the bends, the alternative is to clean chemically.

For offline mechanical cleaning, it is limited by accessibility. U-bends with radii smaller than 4 tube diameters, shell sides of bundles in which the space between the tubes is less than 6.35mm (~1/4 in) and shell sides of fixed-tubesheet units are the surfaces that are inaccessible for mechanical cleaning.

Commercial equipment for offline cleaning inside tubes is driven by compressed air, electricity, or water power and may be provided with water flushing. The drill heads and brushes are used in combinations recommended by their manufacturers to suit the fouling. Three general types of cleaners are commercially available, mostly for cleaning inside tube: (1) cleaners with internal motors, (2) cleaners with external drives or “drill type” cleaners, and (3) blowguns.

CHAPTER 3: METHODOLOGY

The approaches used to identify and characterize the corrosion products are illustrated in Figure 3.1 below.

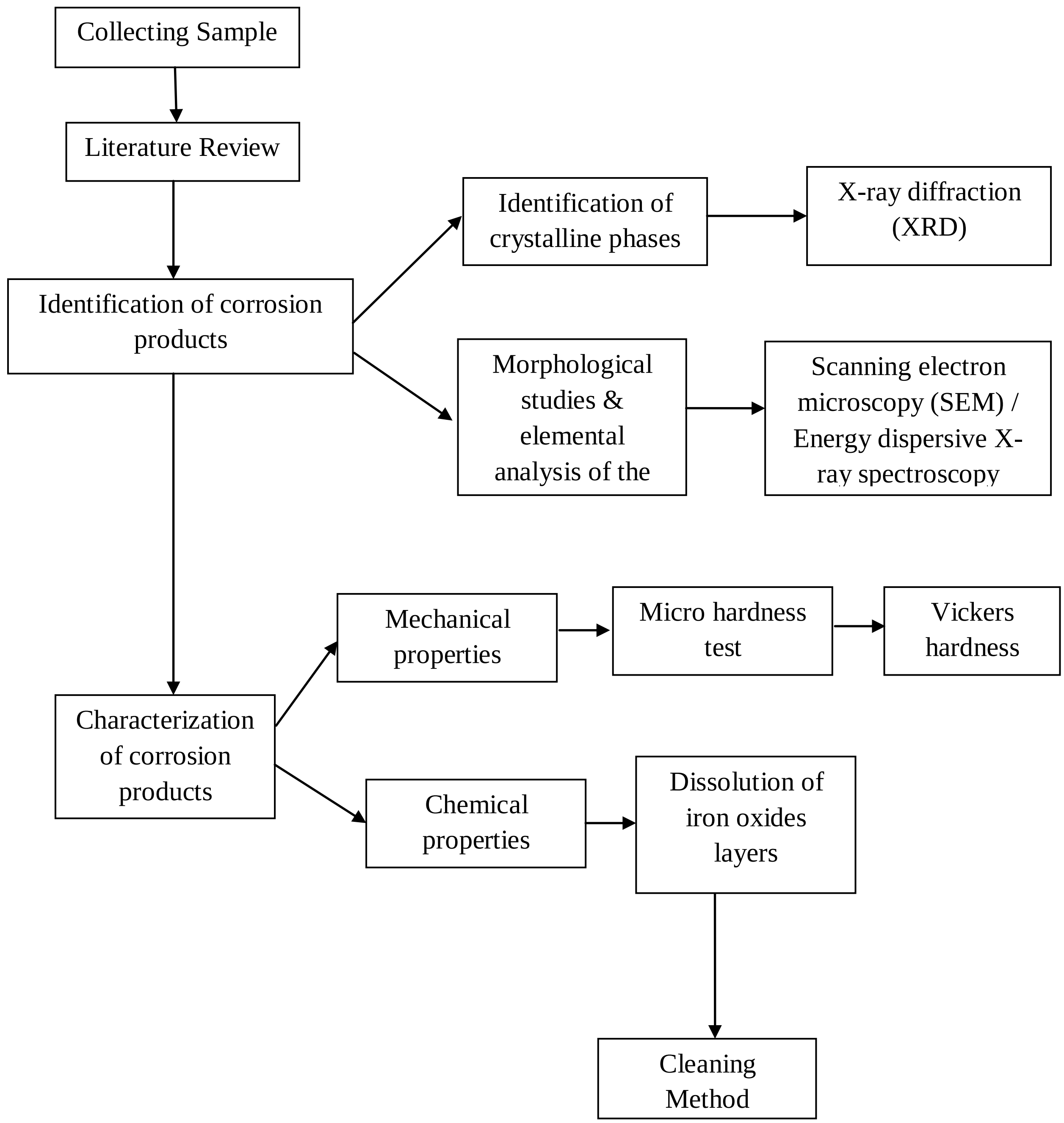


Figure 3. 1: The flow chart of the project

3.1 Collecting Sample

A sample of shell and tube heat exchanger tube is taken from one oil refinery plant (PETRONAS Penapisan Melaka Sdn. Bhd.) located in the peninsular of Malaysia. The service of this heat exchanger is cooler heat exchanger, which means the cooling water is used as its cooling medium. The brief description of the sample and the water treatment system are described in appendix 1 and 2 respectively.

3.2 Literature Review

Thorough literature view is done on mechanisms of cooling water corrosion, identification and characterization of corrosion products and current cleaning methods for internal cleaning of heat exchanger tubes. This cleaning method includes both mechanical and chemical cleanings.

3.3 Identification of Corrosion Products

The techniques used to characterize the corrosion products were XRD (for identification of crystalline phases), SEM/EDX (for morphological studies and elemental analysis of the surface). The preliminary procedure for identification of corrosion products is attached in Appendix 3.

Figure 3. 2: Equipments used for FESEM and EDX analysis at Centralized Analytical Laboratory in UTP

Figure 3. 3: XRD machine at Block 17 in UTP

3.4 Characterization of Corrosion Products

To characterize the mechanical properties of the corrosion product on the internal tube of heat exchanger, one type of Micro hardness which is Vickers test is done. For chemical properties, the corrosion products will be dissolved in chemical solvent and eventually will lead to the next steps which are the cleaning methods. The preliminary procedure for Vickers micro hardness test is attached in Appendix 4.

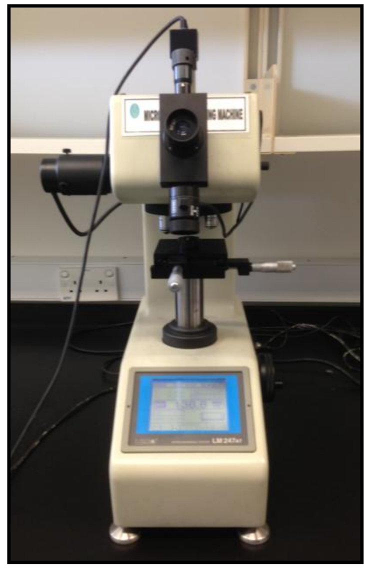


Figure 3. 4: Vickers microhardness indentation equipment at Block 17 in UTP

For the characterization of the chemical properties of the internal corrosion product of heat exchanger tube, the samples underwent several cleaning methods (first stage cleaning) which are immersion in used and new industrial Fovac F315 Rust Remover, Decon 90 cleaning agent and ultrasonic cleaning with deionised water. While for the second stage cleaning, the most effective cleaning agent from the first stage is reused. The only difference is the size of the sample is much larger compare to the first stage and most likely to simulate the cleaning of heat exchanger tube in oil refinery plant. The preparation of heat exchanger samples for both stage of cleaning are attached in Appendix 5.

3.5 Gantt Chart

The overall activities during FYP II are summarized as in Gantt chart below.

Table 3. 1: Gantt chart for FYP II

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Project Work Continues -Identification of corrosion products by FESEM, EDX, XRD -Characterization of mechanical properties of corrosion scale by Vickers micro hardness.								Mid-semester break							
2	Submission of Progress Report															
3	Project Work Continues -Characterization of chemical properties of corrosion scale -Investigate the effectiveness of the cleaning solution.															
4	Pre-SEDEX															
5	Submission of Draft Report															
6	Submission of Dissertation (soft bound)															
7	Submission of Technical Paper															
8	Oral Presentation															
9	Submission of Project Dissertation (Hard Bound)															

Suggested milestone

Process

CHAPTER 4: RESULTS AND DISCUSSIONS

The sample of the heat exchanger tube is ¾ inches outer diameter and made of SA-214 carbon steel. Based on SA-214, Standard Specification for Electric-Resistance-Welded Carbon Steel Heat-Exchanger and Condenser Tubes, they alloying elements of this tube are Carbon (0.18% max), Manganese (0.27-0.63%), Phosphorus (0.035% max) and Sulfur (0.035% max).

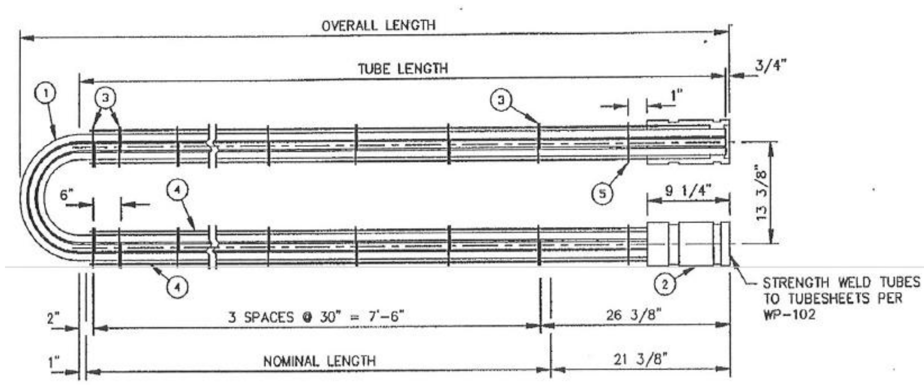


Figure 4. 1: Specification drawing of the heat exchanger tube

Figure 4. 2: The sample of heat exchanger tube used in the project

4.1 Identification of crystalline phases

From the outputs of XRD machine, the results are later been matched with the database library in the software to seek and match the peak. Figure 4.3 show iron oxide

Fe_2O_3 and lepidocrocite γ-Fe_2O_3 / $Fe_2O_3.H2O$ / Fe + 3O(OH) found at peak 2Θ at 4^O and 14^O respectively.

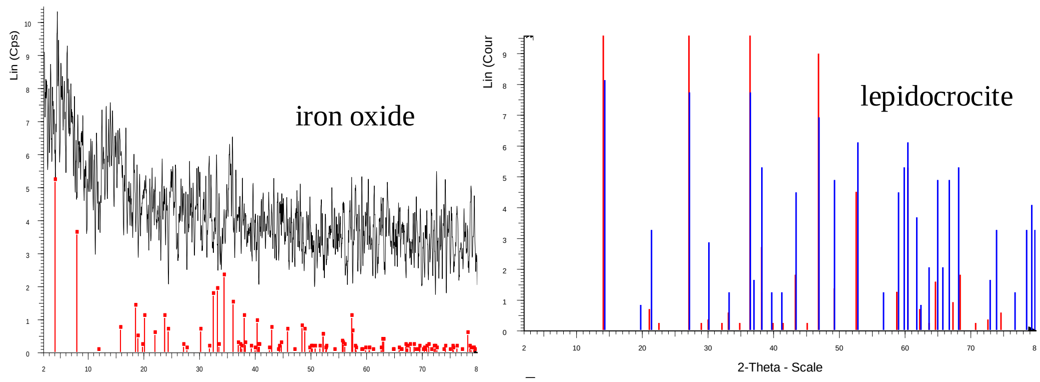


Figure 4. 3: Iron oxide and lepidocrocite found at peak 2-Theta at 4^O and 14^O

Next, Figure 4.4 show hematite α-Fe_2O_3 are found at peak 2Θ at 54^O and 33^O, goethite α-FeOOH / $Fe_2O_3.H2O$ and magnetite Fe_3O_4 are found at peak 2Θ at 22^O, 37^O and 36^O respectively.

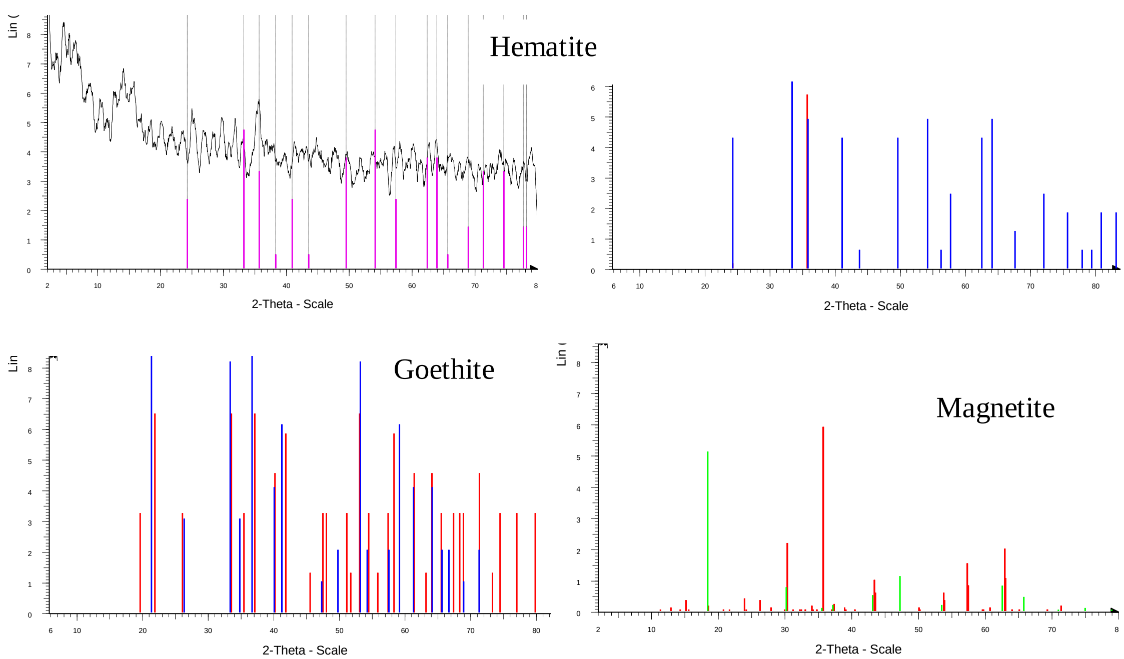


Figure 4. 4: Hematite found at peak 2-Theta at 54^O and 33^O, Goethite and magnetite found at peak 2-Theta at 22^O, 37^o and 36^O

Next, the rust powder is dried at $60^{O}C$ for two hours in the oven. The results from the XRD analysis are as below. Lepidocrocite γ-FeOOH, iron oxide hydroxide FeOOH and hematite α-Fe_2O_3 are found at peak 2Θ at 14^{O}, 14^{O} and 36^{O} respectively.

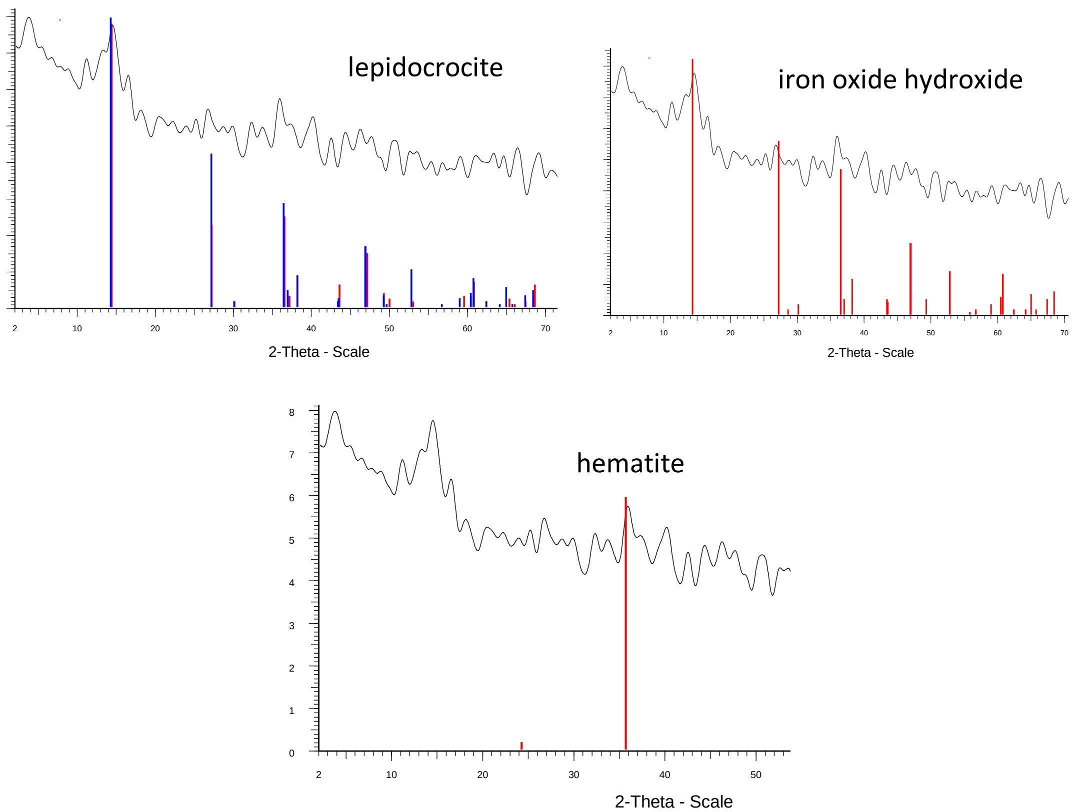


Figure 4. 5: Lepidocrocite, iron oxide hydroxide and hematite found

4.2 Morphological studies & elemental analysis of the corrosion scale surface

From the Field Emission Scanning Electron Microscopy (FESEM), two (2) corrosion products that have been found are Goethite (cotton ball structure) and Lepidocrocite (fine crystal plate structure).

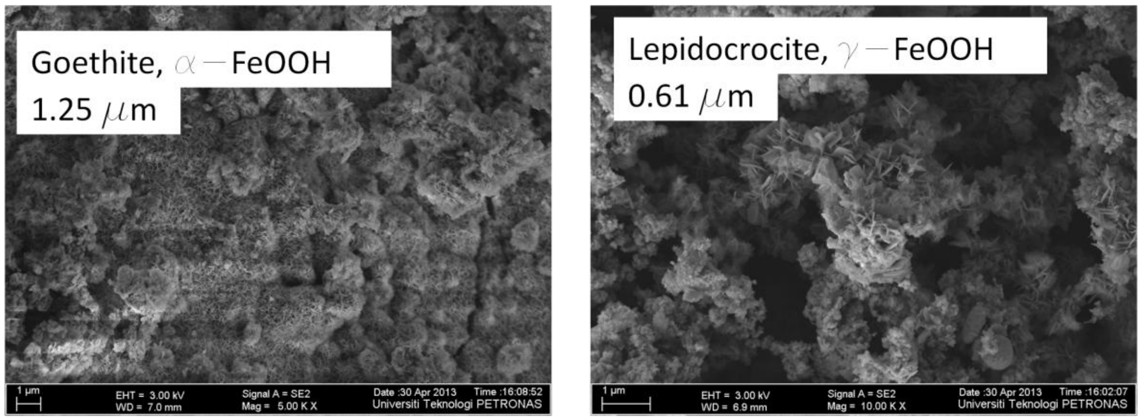


Figure 4. 6: Goethite (cotton balls) and lepidocrocite (fine plate crystal) are found from FESEM.

The mechanical defects also have been found on the surface of the corrosion scale which are cracking and flaking. These defects expose the metal to the corrosive environment, thus increase the corrosion rates of the heat exchanger tube.

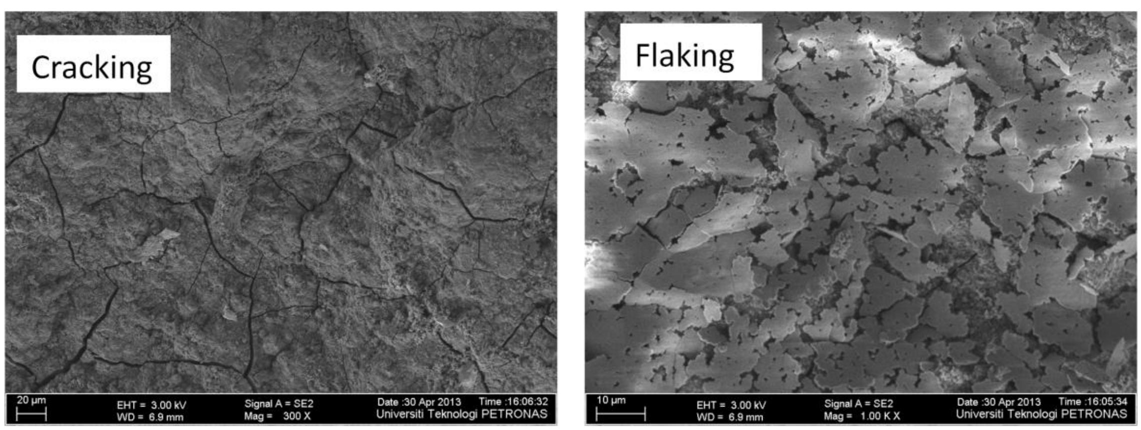
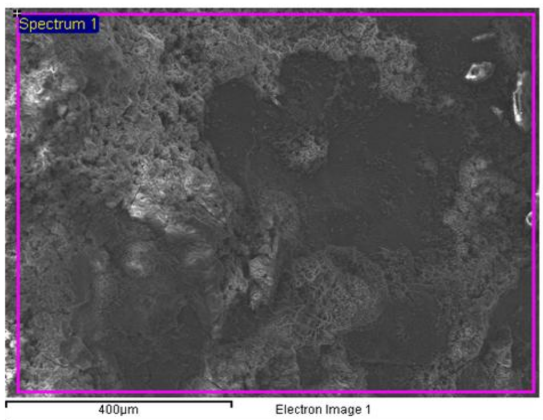


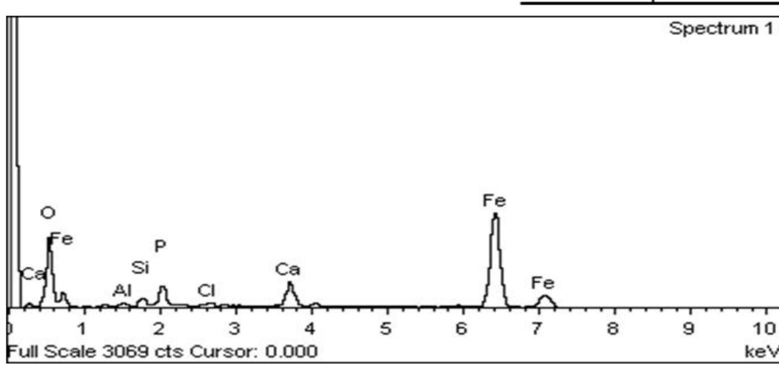
Figure 4. 7: Cracking and flaking found on the surface of corrosion scale

The elemental analysis is done by EDX. The results are as in the table below. The main components of rust which are Iron (Fe) and Oxygen (O) are found. However, due to the limitation of the X-ray machine, light elements such as Hydrogen (H) cannot be detected. The rest of the elements were originated from the alloying elements of SA-214 heat exchanger tube and elements came from the cooling water itself.

Table 4. 1: EDX analysis of corrosion scale



Element	Weight%	Atomic%
O K	31.52	59.13
Al K	0.62	0.69
Si K	1.38	1.47
P K	4.06	3.94
Cl K	0.64	0.54
Ca K	4.85	3.63
Fe K	56.92	30.59
Totals	100.00	

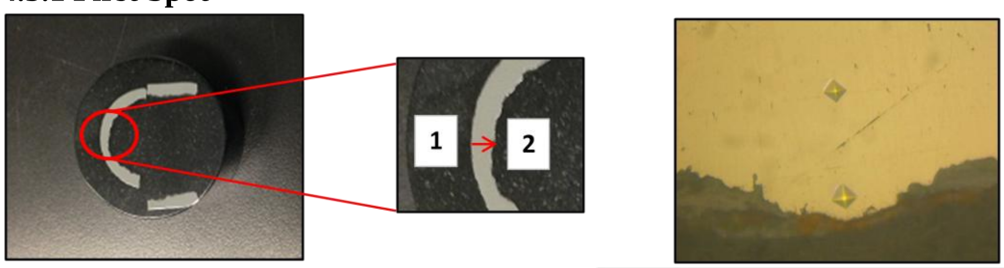


4.3 Characterization of Mechanical Properties of Rust Scale

To maximize the accuracy of point of indentation on the oxide layer, the closest point to it is chosen. The tests are carried out with 25gf indentation force and 10 seconds dwelling time. Based on the three (3) spots examined, the best microhardness value is 110HV.

Based on Metal Ravne [20], the HV values can be converted to tensile strength. Hence, 110HV is equivalent to 350 N/mm^2 or 350 Mpa. Hence, for the effective cleaning of internal heat exchanger tubes, the pressure required for the hydrojet cleaning shall be greater than 350 Mpa or 3,500 Bar. This value is quite high since for the safe use of high-pressure water jetting equipment, local regulations will determine the level at which the term high-pressure (entailing certain restrictions or special procedures) is applicable; generally, this is 10 Barg. However, based on PTS Technical Specification [21] , for ultra high pressure (UHP) water jetting, it is now possible to attain pressures as high as 2,700 bar with flow rates of about 16 l/min. Such systems are remotely operated and track mounted using rigid lances.

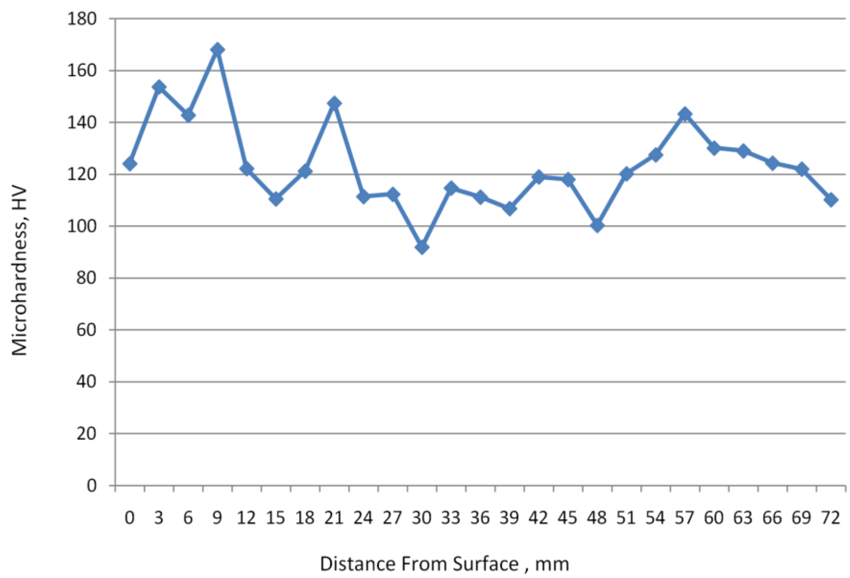
4.3.1 First Spot



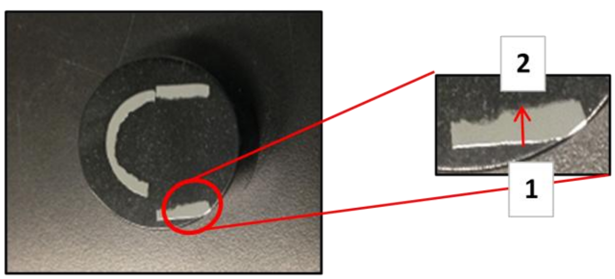
500 magnification of OM (50 lense X 10 eyepiece)

Table 4. 2: Indentation result for the first spot

Distances From Surface , μm	HV	Distances From Surface , μm	HV
0	124.1	39	106.8
3	153.7	42	119
6	142.8	45	118
9	168.1	48	100.3
12	122.2	51	120.2
15	110.5	54	127.5
18	121.2	57	143.3
21	147.4	60	130.1
24	111.4	63	129
27	112.3	66	124.3
30	91.9	69	122
33	114.7	72	110.2
36	111.2		



4.3.2 Second Spot



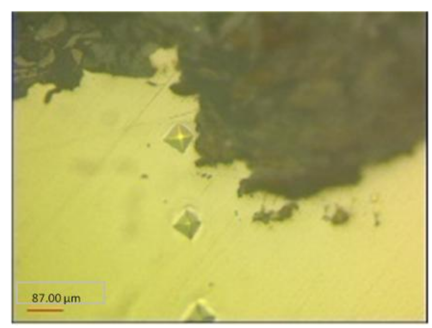
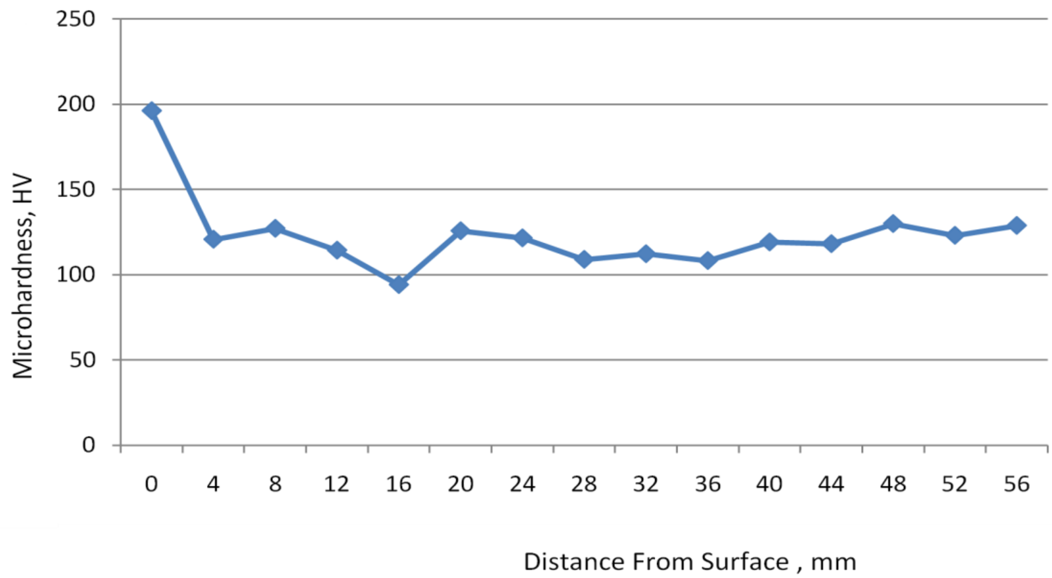


Table 4. 3: Indentation result for the second spot

Distances From Surface , μm	HV	Distances From Surface , μm	HV
0	196.1	32	112.2
4	120.7	36	108.2
8	127.1	40	119.1
12	114.3	44	118.1
16	94.1	48	129.9
20	125.7	52	123
24	121.5	56	128.8
28	108.9		



4.3.3 Third Spot

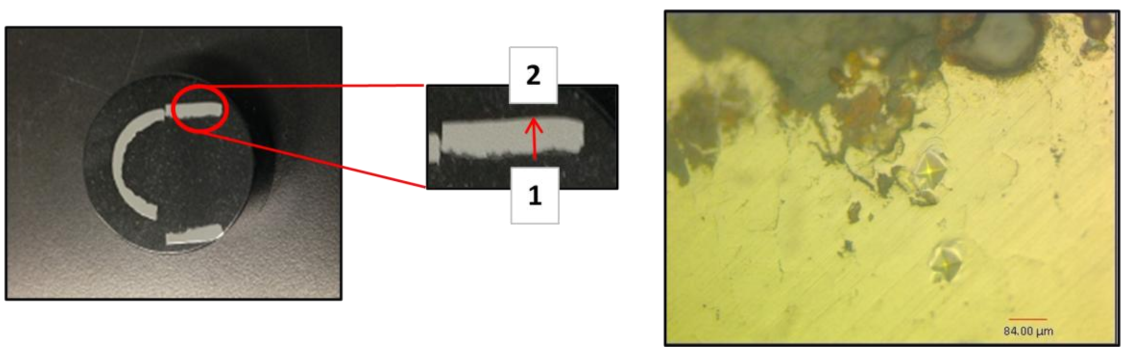
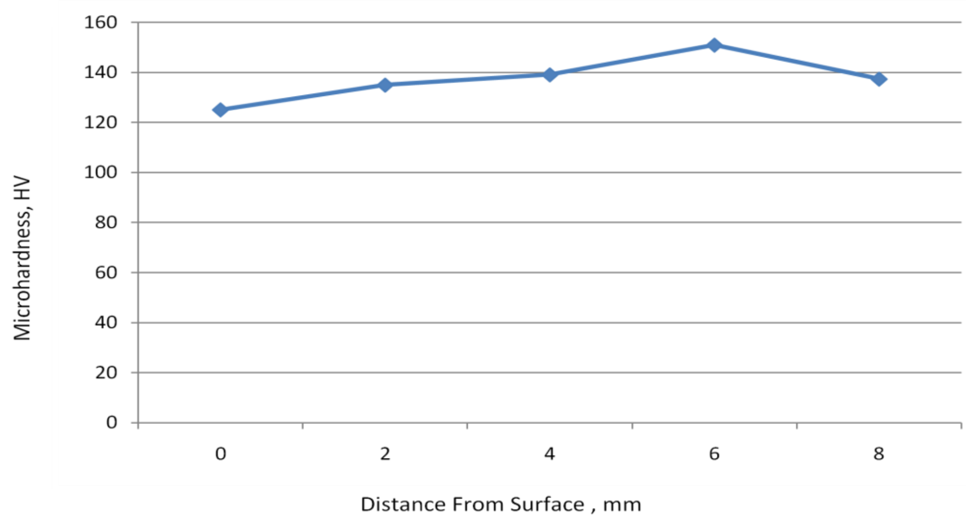


Table 4. 4: Indentation result for the third spot

Distances From Surface , μm	HV
0	125
2	134.9
4	139
6	150.9
8	137.3



4.4 Characterization of Chemical Properties of Rust Scale

For chemical properties of the corrosion scale, it has been characterized with the best cleaning method which probable to remove the corrosion scale from the internal heat exchanger tube. Among the test carried out are immersion test with Fovac F315 Rust Remover, Decon 90 and ultrasonic with deionised water and ultimately, it is found that the best and efficient cleaning agent is Fovac F315 Rust Remover.

<u>First stage cleaning</u>

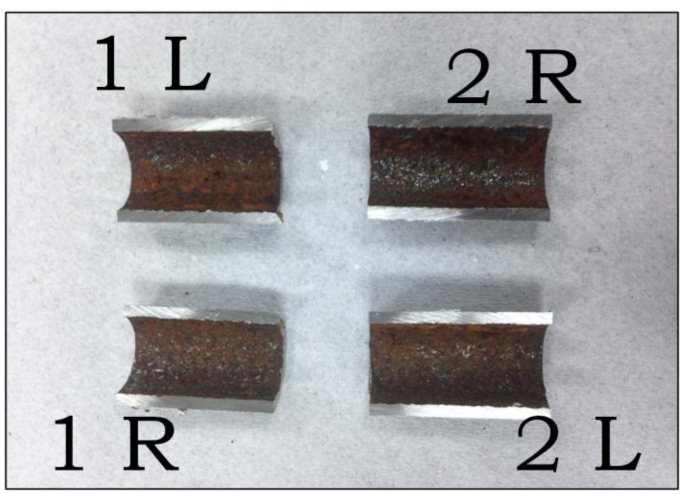


Figure 4. 8: Original condition of the rust scale

Sample 1L

Method: Immersion with used rust remover
Result: Dissolution of rust after 4 hours


Sample 1R

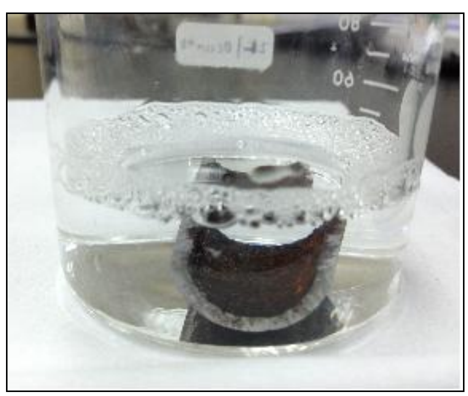
Method: Ultrasonic (immersion in deionised water)

Result: No changes occur on the corrosion scale.

Sample 2L

Method: Immersion with Decon 90 (5% Decon 90 out of overall solution) + Ultrasonic

Result: No changes occur on the corrosion scale.




Sample 2R

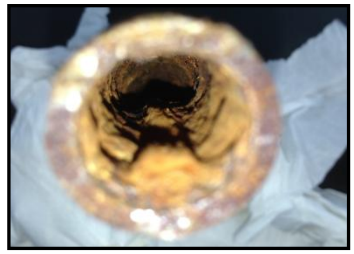
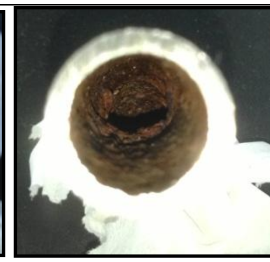
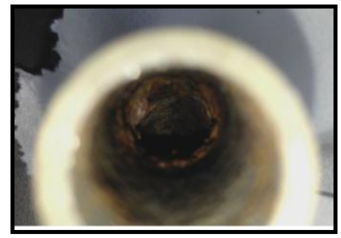
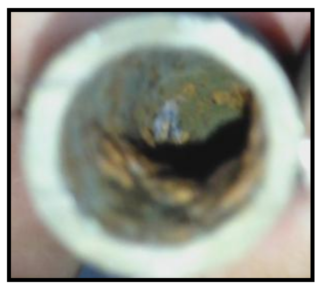
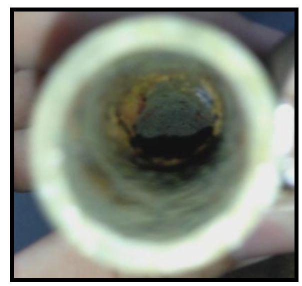
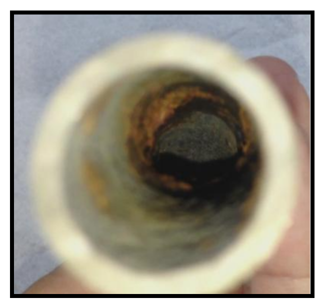
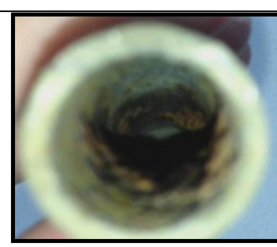
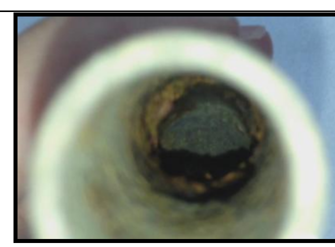
Method: Immersion with new diluted rust remover (1/3 F315 Rust Remover out of overall solution)

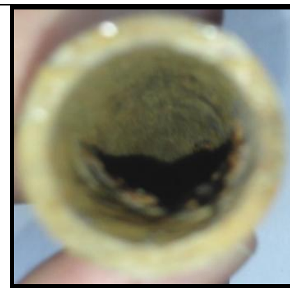
Result: Dissolution of rust after 2 hours

Mass loss = 0.1g

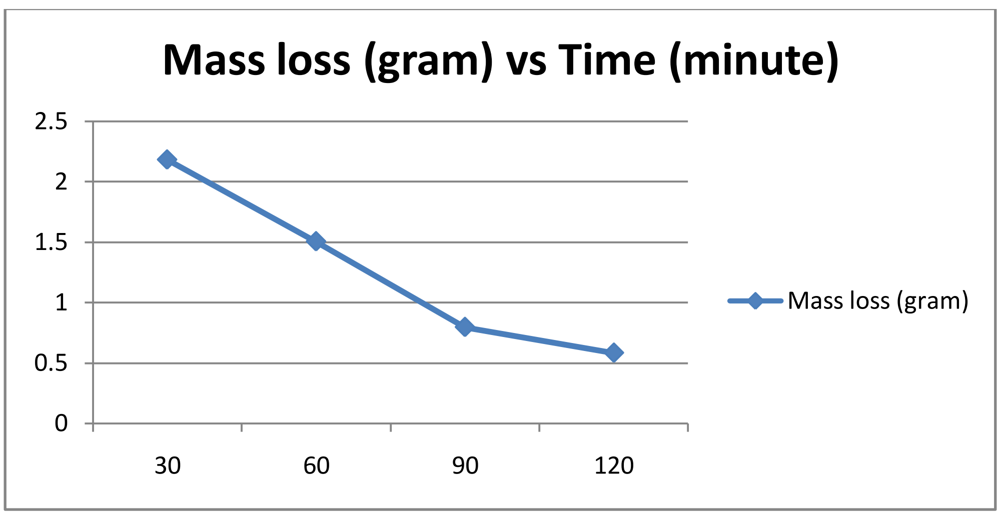
Second stage cleaning

No.	Stage	Description	Condition of internal corrosion (A-left, B-right)
1	- Clean with tap water + mechanical cleaning using brush	Initial mass = 126.1383 g Final mass = 124.1464 g	

			 
2.	- Cleaning by immersion in F315 Rust Remover (50% concentrated) - Clean, dry and mass.	Initial mass = 124.1464 g Final mass = 121.9657 g Time = 30 minutes	 
3.	- Cleaning by immersion in F315 Rust Remover (50% concentrated) - Clean, dry and mass.	Initial mass = 121.9657 g Final mass = 120.4615 g Time = 30 minutes	 
4.	- Cleaning by immersion in F315 Rust Remover (50% concentrated) - Clean, dry and mass.	Initial mass = 120.4615 g Final mass = 119.6665 g Time = 30 minutes	 
5.	- Cleaning by immersion in F315 Rust Remover (50% concentrated) - Clean, dry and mass.	Initial mass = 119.6665 g Final mass = 119.0844 g Time = 30 minutes	 
6.	- Cleaning by immersion in F315 Rust	Initial mass = 119.0844 g	

	Remover (50% concentrated) - Clean, dry and mass.	Final mass = 116.5879 g Time = 180 minutes	 

Time	Mass (g)	Mass loss (g)
0	124.1464	0
30	121.9657	2.1807
60	120.4615	1.5042
90	119.6665	0.795
120	119.0844	0.5821



From the result of the second stage cleaning, the dissolution of the rust scale due to FOVAC F315 Rust Remover is reliable until 120 minutes. Beyond that, the cleaning agent starts to consume the base metal.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

Based on the identification of corrosion products by using XRD machine, the crystalline phases and compounds found are Iron oxide Fe_2O_3, Hematite α-Fe_2O_3, Lepidocrocite γ-Fe_2O_3 / Fe_2O_3.H2O / Fe + 3O(OH), Goethite α-FeOOH / Fe_2O_3.H2O and Magnetite Fe_3O_4. Moreover, Goethite α-FeOOH (cotton ball), Lepidocrocite γ-FeOOH (fine crystal plate), cracking and flaking are found with Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX) approved the existence of their elements. For the recommendation, the corrosion simulation of internal heat exchanger tubes due to cooling water might be carried out to find better results especially for XRD patterns; however this process will be time consuming.

The mechanical properties of the rust scale are examined with Vickers micro hardness test and the hardness value found is 110HV. For the recommendation, the hardness value of the corrosion scale can be identified with more sophisticated techniques such as nano-indentation. Beside indentation hardness, surface roughness and elastic modulus can be found as well. Other techniques to characterize the mechanical properties such as corrosion scale layer profile and surface topography analysis can be done with Infinite Focus Microscopy (IFM). However, the costs for nano-indentation and IFM techniques are quite expensive.

For recommendation on characterization of chemical properties of corrosion products or the cleaning method, the author would like to suggest that the whole tube bundle unit of shell and tube heat exchanger to be used for immersion chemical cleaning testing to see the effectiveness of Fovac F315 Rust Remover. However, the simulation of this cleaning might create few unfavourable problems such as logistic and financial issues.

In conclusion, the project has achieved successful cleaning of internal heat exchanger tube by Fovac F315 Rust Remover.

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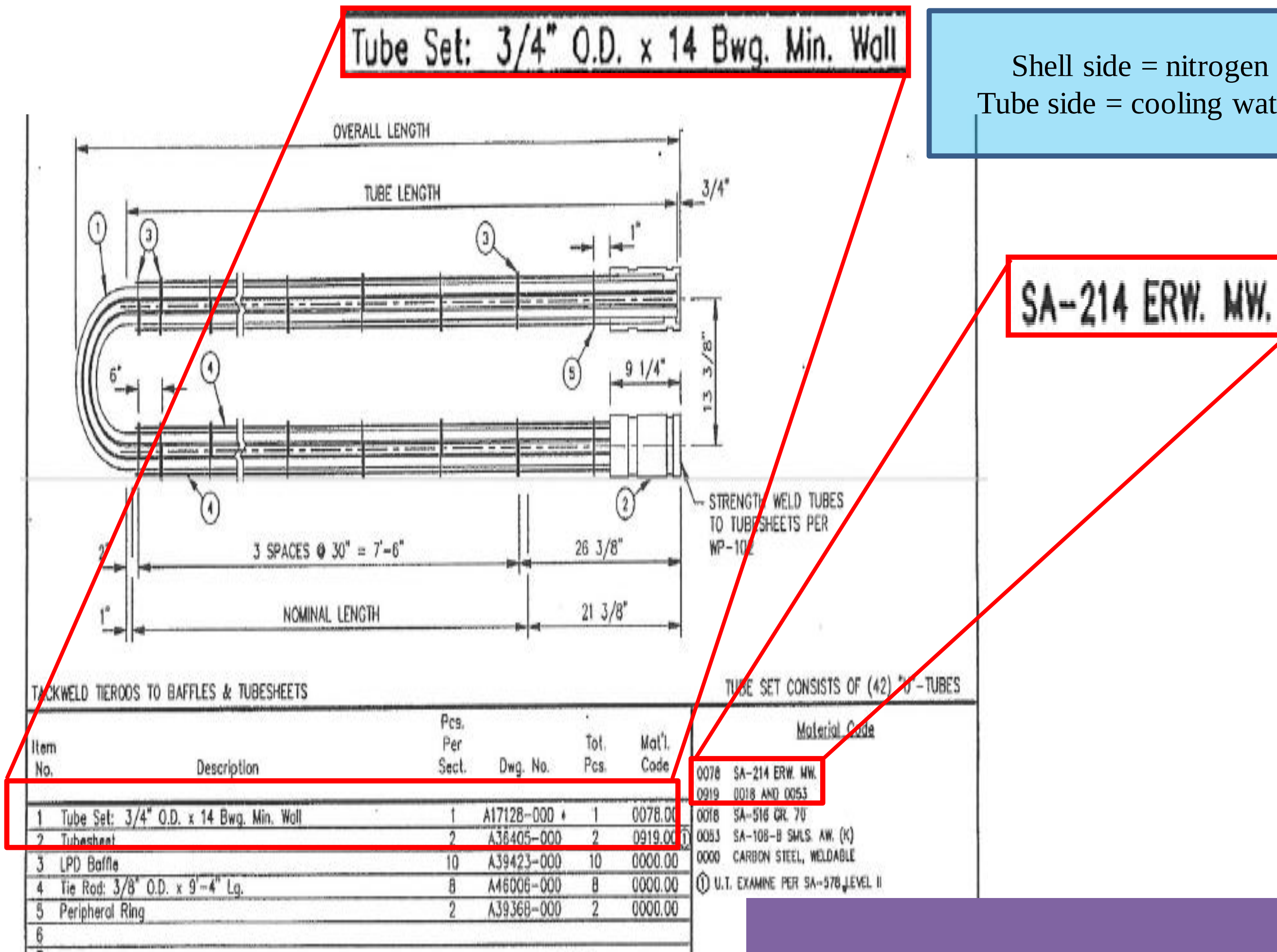
Appendix 1 -Description of sample (HE tube)

Shell side = nitrogen
Tube side = cooling water



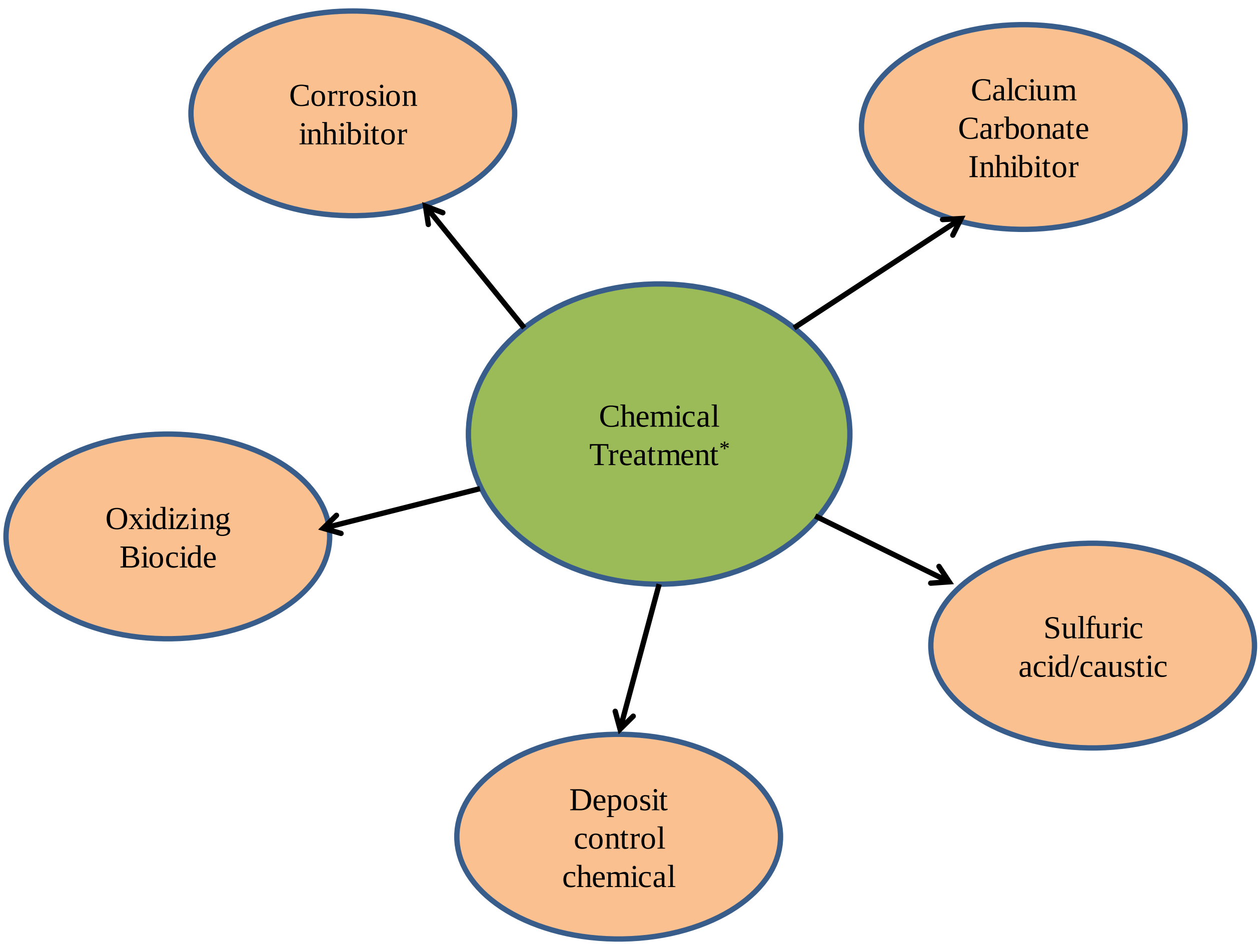
	Shell	Tube
Design Pressure (kg/cm^2G)	41	15
Operating Pressure (kg/cm^2G)	0.8	2.6
Design Temperature (^oC)	150	120
Operating Temperature (^oC)	38	45

Chemical composition (SA-214)*

Carbon, max %	0.18
Manganese, %	0.27-0.63
Phosphorus, max %	0.035
Sulfur, max %	0.035

*Standard Specification for Electric-Resistance-Welded Carbon Steel Heat-Exchanger and Condenser Tubes

Appendix 2 -Description of treatment to cooling water system



*The details of chemical treatment program for cooling water system are attached on the next page

PSR-1 CHEMICAL TREATMENT PROGRAM FOR COOLING WATER SYSTEM

PSR-1 cooling water system is using the following chemical for its chemical treatment program.

1) The main chemical treatment for the cooling system consists of:

- **DN2250A** - as corrosion inhibitor (Phosphate base)
- **Gengard GN8102** - combines non-phosphorus, Alkyl Epoxy Carboxylate (AEC) calcium carbonate inhibitor and a stress tolerant polymer (STP) to provide complete deposition and scaling control for highly supersaturated waters over the alkaline pH range of 7.8 to 9.0

This treatment concept maximizes corrosion protection using DN2250A while controlling deposition and scaling by using Gengard.

The treatment relies upon a polymeric dispersant to keep relatively high levels of phosphate in solution, thus providing this corrosion protection.

- DN2250A & Gengard GN8102 contains:
  - Orthophosphate for anodic corrosion control
  - Polyphosphate for cathodic pitting control
  - Halogen Resistant Azole (HRA) for copper alloy corrosion control
  - STP polymeric dispersant

2) Sodium hypo-chloride as oxidizing biocide. This will ensure microbe in the cooling water is under control. The injection is continuous and the range is 0.2 -0.5 ppm of free residual chlorine.

3) Slug dosed of non-oxidizing biocide (NX1100/1103). This is supplementary biocide to assist sodium hypo-chloride. This non-oxidizing normally injected once a week.

4) Deposit control chemical - to prevent deposition of sludge inside the system.

5) Sulfuric acid/caustic - as pH control method.

The treatment above will be monitored using routine lab sampling and adjustment will be done if any parameters below are off spec. The following is the main parameters being monitored for CW system:

Parameters	Unit	Target range
pH		8-9
PO_4	ppm	8-14
Delta PO_4	ppm	< 3
Conductivity	us/cm	<2500
Iron	ppm	<1
Calcium	ppm	<250
Silica	ppm	<200
FRC		0.2-0.5
TBC	CFU/ml	<1000
Corrosion rate (MS)	mpy	<1
Corrosion rate (admiralty)	mpy	<0.8

APPENDIX 3: PREPARATION FOR SEM / XRD

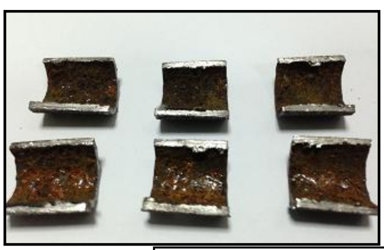
1) The sample of heat exchanger tube

2) The sample is divided into three sections, 20mm each

3) The outer diameter is taken, ~ 19.4mm

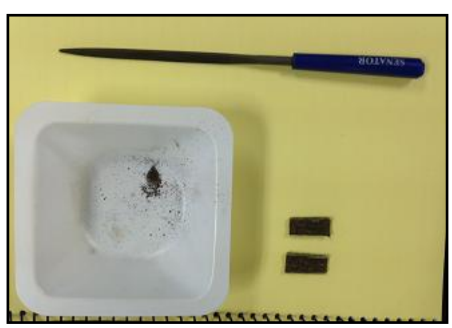
4) The sample is named as A, B and C and been cut.

5) Each section is cut into half and named as A1, A2, B1, B2, C1 and C2.



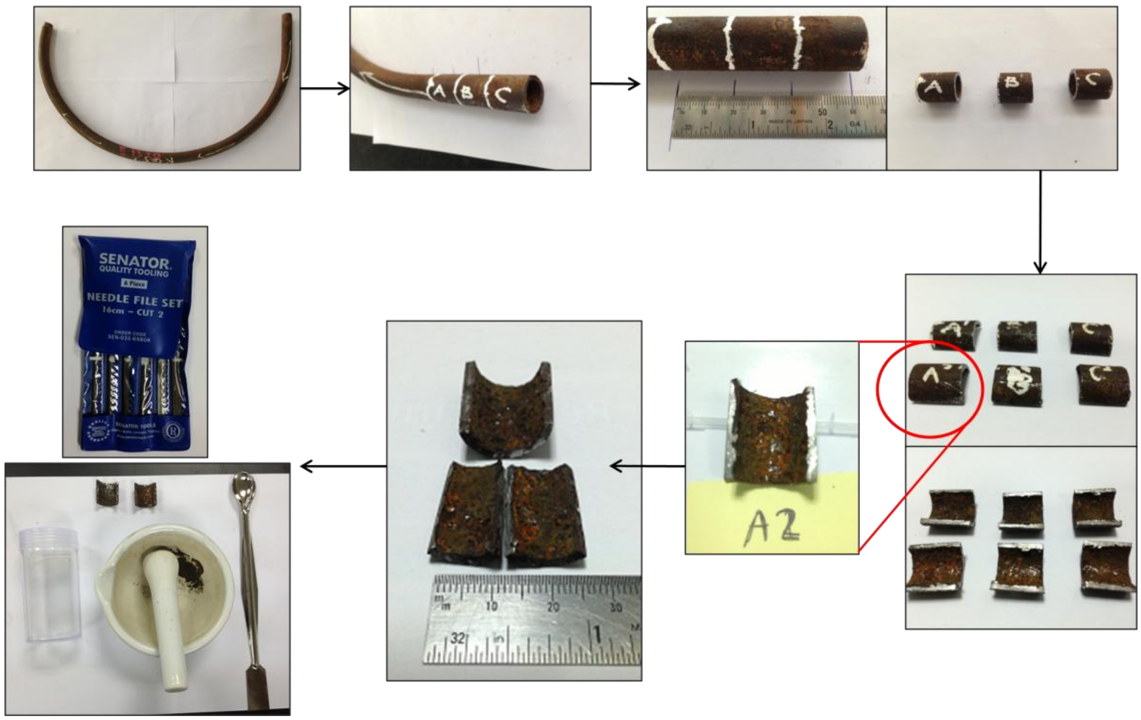
6) The pictures of corrosion scale of inner tube.

7) B2 is cut into three segments. This is for XRD since flat surface is mandatory.



8) B2 segments are been extracted to powder form. This is alternative since the segment doesn't show any positive result in XRD

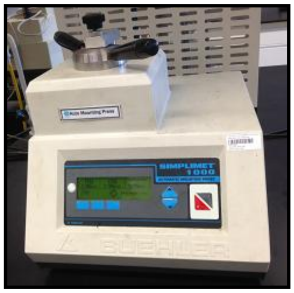
[Continue] APPENDIX 3: PREPARATION FOR SEM / XRD



<u>Checklist on the sectioned segments of the heat exchanger tube</u>

Segment	Part	Description
A	A1	Reserved for Vickers micro hardness test
	A2	Cut into two. One half is use for FESEM & EDX
B	B1	Both parts are used for XRD. Abrasion tools are used to scrap the rust scale into powder forms. Later the powder is grounded into fine powder forms.
	B2	
C	C1	Both parts are used for XRD. Abrasion tools are used to scrap the rust scale into powder forms. Later the powder is grounded into fine powder forms. After that, the rust powder is dry in oven at 60^{O}C for 2 hours.
	C2	

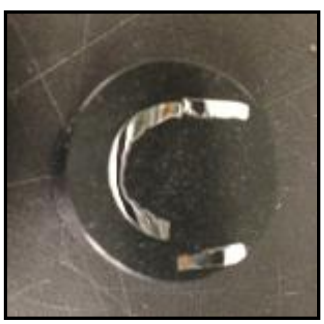
APPENDIX 4: PREPARATION FOR VICKERS MICRO HARDNESS TEST



1) A1 segment are hot-mounted. Phenolic powder which is thermosetting polymeric powder is placed in a mould with the sample to which heat and pressure is applied.

2) The mounted sample is grinded manually. Start with 320 grit SiC paper, then 400, 600 and 800 grit.

3) The mounted sample is polished with alumina suspension. Start with 0.3 micron then finish with 0.05 micron of alumina.



4) The mounted sample is polished until mirror-like image is appearing.

5) The mounted sample is etched with 2% Nital etchant to ensure the grain boundary can be seen under microscope.

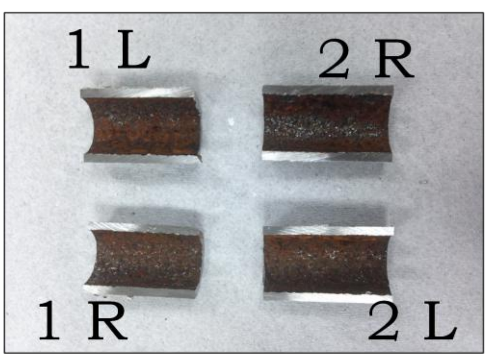
6) The mounted sample is ready for Vickers micro hardness test.

APPENDIX 5

<u>Sectioning for the first stage of cleaning (Sample 1R, 1L, 2R and 2L)</u>

One portion (60mm) of the tube is sectioned

The sectioned part is further cut into two (2) parts, 1 and 2. Later, both parts are cut into half as 1R, 1L, 2R and 2L.

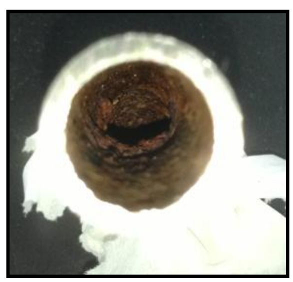


<u>Sectioning for the second stage of cleaning</u>

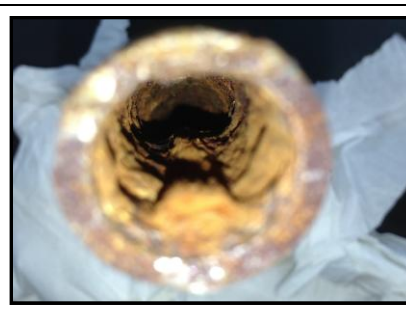
Striped mark on the heat exchanger tube show the portion which is needed to be cut.

Three (3) cm length for each mark.

The sectioned sample is 15cm length. (approximately)



Internal corrosion on part B



Internal corrosion on part A